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13. ABSTRACT (Maximum 200 words)

The goals of this research were to study specific defect configurations in $Hg_{0.79}Cd_{0.21}Te$ (MCT), using perturbed angular correlation (PAC) measurements, with emphasis on the defect consisting of vacancies trapped at the donor impurity indium; secondarily, to study antisite defects and small indium precipitates. The first of these objectives was met with the identification and structural characterization of $In-V_{Hg}$ complexes. It was determined that this defect does occur under appropriate conditions (reported in several publications), and that it consists of an indium impurity on a cation site, joined to a single vacancy at the $\langle 110 \rangle$ next nearest site. The mysterious $\langle 111 \rangle$ orientation of the electric field gradient (EFG) observed for donor-vacancy complexes in MCT and other II-VI semiconductors was shown to result from the polarization of Te atoms surrounding the indium donor. The thermodynamics of the mercury vacancy and indium-vacancy complexes were extensively characterized, resulting in good estimates of the migration energy for Hg vacancies and binding energies for vacancy-indium pairs. $In-V_{Hg}$ complexes were seen to interact with H impurities. No evidence of either antisite defects or small metal clusters was seen at doping levels up to 10^{17} In/cm^3 .

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FINAL REPORT

M. L. SWANSON, PI

30 SEPTEMBER 1993

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DEPARTMENT OF PHYSICS AND ASTRONOMY
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The purpose of this project has been to characterize the interactions between indium donors and mercury vacancies in the infrared material, $Hg_{1-x}Cd_xTe$. (MCT). These characterizations used the perturbed angular correlation (PAC) technique. This technique is a nuclear hyperfine spectroscopy similar to Mössbauer spectroscopy. The interaction most frequently used is the one between the quadrupole moment of the probe nucleus and the local electric field gradient (EFG). Since this interaction decreases as r^{-3} , it is particularly sensitive to nearby point defects such as trapped vacancies. PAC consists of observing the angular correlation between successive gamma rays emitted from a probe nucleus, in this case ^{111}In . This angular correlation can be expressed in a function $R(t)$ which is a measure of the time dependence of the anisotropy between the two gamma rays. By fitting the measured $R(t)$ to a theoretical function, several parameters may be determined:

- the absolute fraction of indium atoms in a particular defect site,
- the strength of the hyperfine interaction, v_Q , which may be used as a label of a particular defect,
- the orientation of the defect EFG with respect to known crystal axes.

Further details on the PAC technique are available in reviews in the literature.¹

The goals of this project were stated as, "To study specific defect configurations in MCT, using perturbed angular correlation (PAC) measurements. The emphasis will be on defect consisting of vacancies trapped at the probe ^{111}In nuclei; antisite defects and small precipitates that contain In will also be studied." The first of these goals was met with the identification of $\text{In}_{\text{Hg}}-\text{V}_{\text{Hg}}$ pairs in MCT. Bulk samples of MCT ($x=0.21$) grown by solid state recrystallization were obtained from Herb Schaake of Texas Instruments. These samples were doped with ^{111}In by annealing in sealed quartz ampoules at 350°C for greater than 6 hours. Controlled etching showed that this treatment was sufficient to diffuse the indium greater than $1\mu\text{m}$ into the material. In samples which were allowed to cool slowly to room temperature from the annealing temperature, the only interaction observed was a low frequency (~5MHz) which was attributed to the indium atoms being on metal sites in slightly strained or alloy-broadened environments. However, when samples were quenched in vacuum from 350°C or above, two significant interactions were observed; $v_{Q1}=83\text{MHz}$ and $v_{Q2}=92\text{MHz}$ (Fig. 1). Subsequent annealing in mercury-saturated conditions removed these interactions; therefore, they were identified as arising from the trapping of mercury vacancies at next-nearest neighbor sites to the indium donors (In-V pairs).

¹ Gary L. Catchen, J. Mater. Educ. 12, 253 (1990).

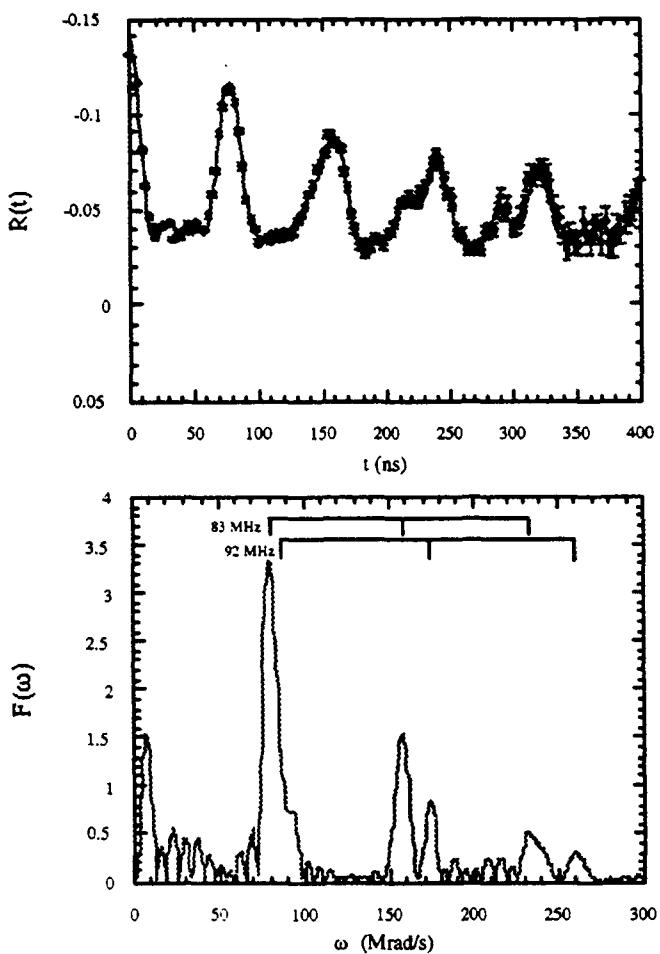


Fig. 1 - PAC spectrum and Fourier transform for ^{111}In in $\text{Hg}_{0.79}\text{Cd}_{0.21}\text{Te}$.

gradient arising from the dipole field will exceed that arising from the monopole field. Calculations of the electric field gradient arising from the vacancy and polarized tellurium ions were performed. These calculations used the polarizability of Te^{2-} ions in the MCT lattice which was calculated by Sohn, et al.² The results of these calculations show that the electric field gradient has a principal axis aligned at 45° from the $\langle 100 \rangle$ axis, close to the observed $\langle 111 \rangle$ alignment. When this orientation is used in fitting the $R(t)$ spectra taken with detectors aligned along the principal crystal axes, the simulated spectra agree with the actual data to within the experimental error of (Fig. 2).

After the In-V pairs were identified, attempts were made to characterize their geometry and thermodynamics. Orientation measurements using PAC showed that the EFG at the indium site, which was caused by the trapping of a vacancy, had a principal axis near to the $\langle 111 \rangle$ crystal axis direction. This orientation was contrary to the assumed defect symmetry of $\langle 110 \rangle$ for the InHg-VHg pair. A polarized point-ion model was proposed in which the tellurium ions nearest to the vacancy were polarized by the electric field due to the vacancy. The electric field gradient at the next-nearest neighbor site (with respect to the vacancy) includes a contribution from the dipole field of the polarized tellurium ions as well as the regular monopole field of the vacancy. In fact, since at least one of these tellurium ions is closer to the next-nearest neighbor site, the contribution of the

² Sang Ho Sohn and Yoshihiro Hamakawa, J. Phys. Soc. of Japan 61, 2538 (1992).

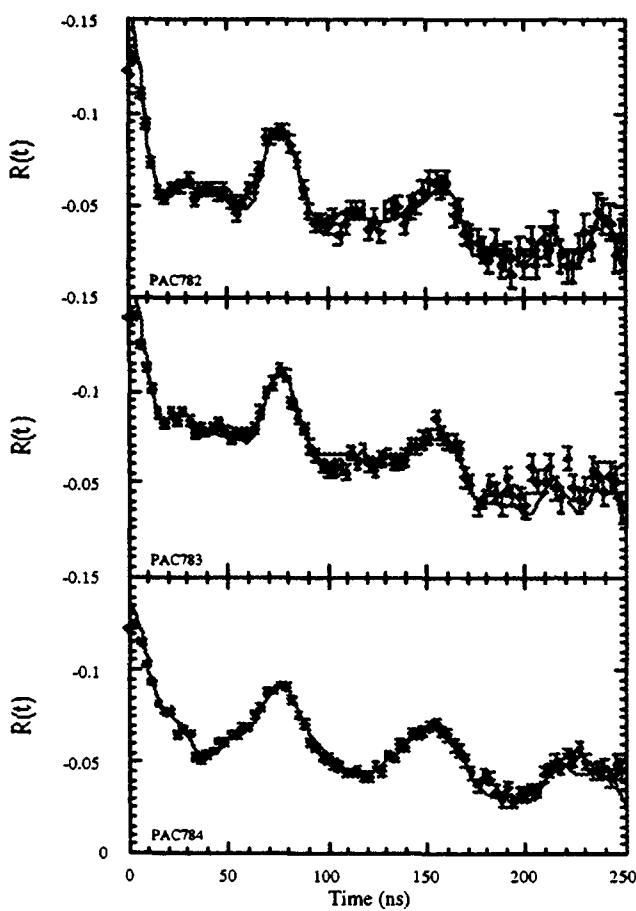


Fig. 2 - PAC spectra of In-V pairs in MCT with detectors aligned crystal axes. (top) $<100>$, (middle) $<110>$, (bottom) $<111>$.

concentration of vacancies after quenching, these vacancies will tend to form more stable In-V pairs or be annihilated at sinks. These two processes are signified by the following chemical equations:



Since the PAC technique enables the measurement of absolute fractions of indium probe atoms in specific defect sites, we were able to determine the thermodynamic behavior of these In-V pairs in MCT as a function of annealing history. It was observed that the fraction of indium atoms participating in In-V pairs increased when the material was annealed at temperatures near 100°C. This increase is caused by the equilibration of the large number of vacancies trapped in the material when it is quenched from 350°C—the vacancy concentration is determined by the higher annealing temperature, while the spatial distribution of these vacancies, particularly with respect to indium impurities, is determined by the lower annealing temperature.

Here, K_1 and K_3 represent the rates of the reactions in the forward direction and K_2 and K_4 represent the rates in the reverse direction. The rate equations for these reactions are therefore,

$$\frac{d[C]}{dt} = K_1[In][V] - K_2[C] \quad (3)$$

$$\frac{d[V]}{dt} = -K_1[In][V] + K_2[C] - K_3[V] + K_4, \quad (4)$$

where $[C]$ is the concentration of In-V pairs, $[V]$ the concentration of free vacancies, and $[In]$ the concentration of unpaired indium atoms.

These equation can be solved in the aftermath of quenching by considering that eqs. (1) and (2) run mainly in the forward direction. In this case, the fraction of indium atoms in pairs (the fraction measured by PAC) was found to be

$$f(t) = 1 - (1 - f_0) \exp \left[-\frac{K_1[V_0]}{K_3} (1 - e^{-K_3 t}) \right]. \quad (5)$$

The time dependence of the PAC fraction was measured for a variety of temperatures between 68°C and 110°C and the results were fitted to the above equation to determine K_3 as a

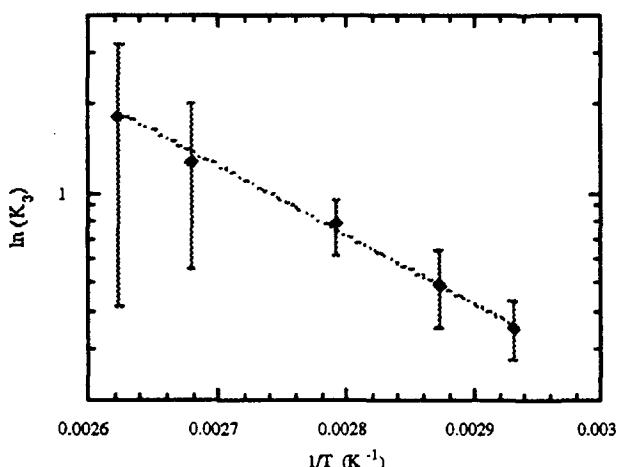


Fig. 3 - Arrehnius plot of the reaction rate K_3 vs. $1/T$.

function of temperature. When $\ln(K_3)$ was plotted versus T^{-1} in an Arrhenius plot (Fig. 3), the activation energy of vacancy migration was found to be $0.45\text{eV} \pm 0.04\text{eV}$. This value is in good agreement with some of the previous experiments which measured the migration energy by other techniques ^{3,4,5}. Equations (3)

³ A. V. Gorshkov, F. A. Zaitov, S. B. Shangin, G. M. Shalyapina, I. N. Petrov, and I. S. Asaturova, Sov. Phys. Solid State 26, 1787 (1984).

and (4) may also be solved in the case where the In-V pairs are dissociating. This occurs in the temperature range between 140°C and 300°C. By using an analysis similar to that above, we determined an In-V pair binding energy of $0.44 \text{ eV} \pm 0.23 \text{ eV}$.

The influence of hydrogen incorporation on the properties of MCT was also studied by PAC. Samples that had been quenched and annealed to create a large fraction of In-V pairs were exposed to boiling water for 4 to 6 hours. After this exposure, the previously observed PAC frequencies of 83 MHz and 92 MHz vanished and were replaced by frequencies of 38 MHz and 45 MHz. It is believed these frequencies were related to the decoration of the In-V pair by hydrogen introduced from the boiling water. This new complex was stable up to 150°C, much like the In-V pairs.

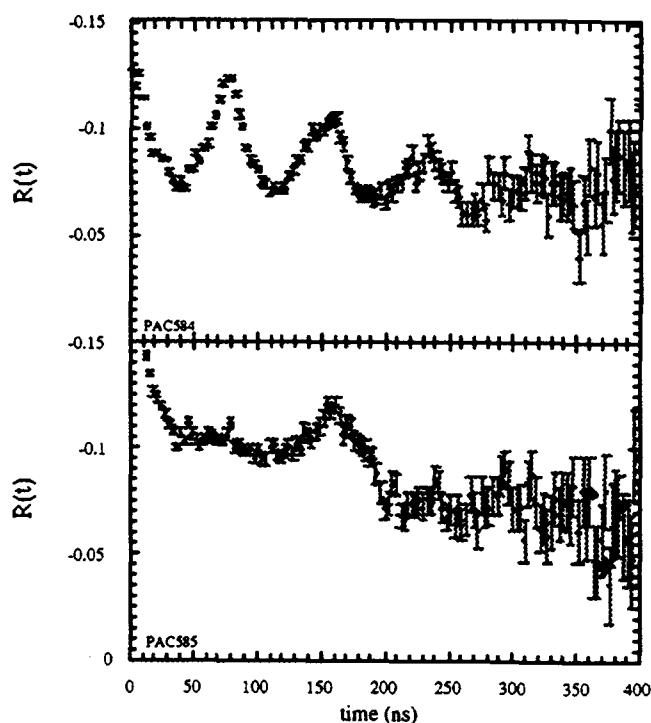


Fig. 4 - Effect of hydrogenation on In-V pairs. (top) PAC spectrum for MCT annealed at 350°C and quenched. (bottom) PAC spectrum for same sample after annealing in boiling water for 4 hours.

acceptors.

Secondary ion mass spectroscopy (SIMS) and ion beam nuclear reaction analysis (NRA) were used to determine if the amount of hydrogen incorporated into the film was

To correlate the formation of these new hydrogen-related defects with the electrical properties of the material, Hall effect measurements were performed. These measurements showed that the introduction of hydrogen by exposure to boiling water had the effect of converting n-type MCT to p-type with hole concentrations of the order of 10^{17} cm^{-3} . This conversion occurred regardless of whether the sample had been annealed at high temperature and quenched. No interaction was observed between the hydrogen and indium atoms which were not already in In-V pairs as might be expected if the hydrogen atoms were acting as

⁴ J. S. Chen, F. A. Kroger, and W. L. Ahlgren, *The Proceedings of the U. S. Workshop on the Physics and Chemistry of Mercury Cadmium Telluride* (1984).

⁵ Mei-Fan Sung Tang and David A. Stevenson, *J. Vac. Sci. Technol. A* 7, 544 (1989)

enough to cause the changes observed. These experiments showed that up to 10^{17} cm^{-3} hydrogen atoms were present in samples which had been annealed in boiling water for 4 hours. The SIMS data showed that oxygen was also incorporated but only to the level of 10^{15} cm^{-3} . Therefore, it seems the electrical effects observed must arise from the hydrogen or some defect introduced along with the hydrogen. While 100°C is usually too low a temperature for the creation of vacancies, it is possible that the chemical reaction of the boiling water with the surface of the MCT has the effect of preferentially removing mercury and helping to create vacancies in this manner. But a suitable explanation for the type-conversion due to exposure to boiling water has yet to be found.

In summary, the research covered in this project had four major results:

- The compensation of indium donors in $\text{Hg}_{0.79}\text{Cd}_{0.21}\text{Te}$ by direct pairing with mercury vacancies was observed.
- The electric field gradient at the next nearest neighbor site to these vacancies was found to be strongly influenced by the polarization of the Te ions surrounding the vacancy.
- The binding energy of the In-V pairs was determined to be 0.35 eV and the migration energy of mercury vacancies was found to be 0.45 eV.
- Large amounts of hydrogen were observed in materials annealed in boiling water. This hydrogen caused the conversion of n-type material to p-type. The decoration of In-V pairs with hydrogen was observed, but no decoration of In donors was evident.

PARTICIPATING SCIENTIFIC PERSONNEL

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ADVANCED DEGREES AWARDED

Ph.D. in Physics - James C. Austin, August 1992.

Ph.D. in Physics - Wm. Christopher Hughes, October 1993.

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Please note that the paper "Hydrogen incorporation in $HgCdTe$ Observed by..." was never published.